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Temperature-Dependent Collection Efficiency of a Cryogenic Trap for Trace-Level Volatile Organic Compounds

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by

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16. ABSTRACT

Reduced temperature preconcentration of volatile organic compounds in a packed trap is examined experimentally as a function of trapping temperatures ranging from -180°C to +100°C. Trapped compounds are thermally desorbed into a capillary column-equipped gas chromatograph and quantified with a flame ionization detector. Data sets are presented for 21 compounds of environmental interest at various concentrations (in dry zero air) in the range of 0.1 ppbv to 100 ppbv. Measured chromatographic peak areas increase from a low but non-zero value for high trap-temperature runs to a constant value as the trap temperature is lowered. Extrapolated Clausius-Clapeyron equations are shown to be a useful guide in estimating the trap temperature required for 99% collection efficiency.

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Temperature-Dependent Collection Efficiency of a Cryogenic Trap for Trace-Level Volatile Organic Compounds

Introduction

Ambient air contains a complex mixture of volatile organic compounds (VOCs) at low concentrations[1,2]. To identify and quantify these compounds accurately at typical concentration levels of one part per billion by volume (ppbv) or less, analytical instruments often require a preconcentration step. In one such technique, ambient air is pulled through a reduced temperature, packed trap where low boiling point compounds condense onto trap surfaces while the major air constituents pass through the system.

The equilibrium case of a vapor above its own condensed phase can be considered as a first approximation to the general case of the residual vapor pressure of a VOC in a cooled trap. Clausius-Clapeyron equations describe this vapor and condensed phase equilibrium, although the temperature range valid for these equations does not include the low temperatures needed for VOC preconcentration. If such equations are extrapolated, a finite vapor pressure is predicted, even at the lowest useable temperature, -183C (boiling oxygen); so that in theory, some material is always lost. However, the extrapolations could be used to estimate the trap temperature required to reduce a target compound's vapor pressure enough to make the losses negligible[3,4].

In this report, temperature-dependent collection efficiency for a specific trap design is experimentally determined for 21 compounds and compared to calculated values to ascertain whether extrapolated Clausius-Clapeyron equations are a useful guide for selecting trap temperatures. Phase changes in the condensed phase, which are expected to reduce vapor pressure below extrapolated values, are not considered explicitly. Additionally, no attempt is made to model gas-surface reactions or synergistic chemical effects with trap materials; however, experimental evidence of such mechanisms is discussed.

Theoretical Development

Data that relate vapor pressure to temperature for VOCs are available for the pressure range of 1 to 760 torr[5], many orders of magnitude above the partial pressures, or concentrations, normally encountered in ambient air. To predict trapping feasibility for a particular compound, such data can be extrapolated to pressures of interest with a mathematical formulation derived from well-known thermodynamic principles, the Clausius-Clapeyron equation[6],

$$\ln(p) = (-L/nR)(1/T - 1/To) + \ln(Po) \qquad \text{(Eq. 1)}$$

where p = pressure

L = latent heat of transformation

n = scaling constant

R = ideal gas law constant

T = temperature

To, Po = known data point (temperature, saturation pressure)

This equation is valid only for a single compound in thermal equilibrium with itself under the phase conditions at To and Po. In theory, it overestimates vapor pressure in the presence of co-trapped compounds and also upon extrapolation to low temperature. Thus, calculations of trapping efficiency based on Equation 1 are expected to be conservative. This is discussed in more detail in Reference 7.

The quantitative experimental data collected yield integrated peak areas for each compound. Consequently, the estimator equation (Equation 1) must be transformed to this format for direct comparisons.

Temperature-dependent pressure information is available for most compounds of interest from the CRC Handbook of Chemistry and Physics[8] in the form of the following empirical relation:

$$\text{Log}_{10}\ (p) = (-0.2185\ A/K) + B \qquad \text{(Eq. 2)}$$

where p = pressure (torr)

K = temperature (K)

A,B = tabulated parameters for each compound.

This equation is identical in form to the theoretical relation presented in Equation 1, except that it is restricted to certain temperature ranges.

First, Equation 2 must be altered to reflect pressure (p) in atmospheres (equivalent to concentration units) and temperature (T) in degrees centigrade:

$$\text{Log}_{10}\ (p) = (-0.2185\ A)/(T + 273) + B - \text{Log}_{10}\ (760) \qquad \text{(Eq. 3)}$$

Then, to convert the pressure units to area counts, assume the following:

(1) incoming concentration, c_i, is known;

(2) detector response, $r = A_t/c_i$, is also known, where A_t = area count for 100% trapping efficiency.

Provided equilibrium is reached, the concentration at the trap exit should be equal to the vapor pressure (p) of the compound in question at the trapping temperature. The peak area is proportional to the amount trapped, which is proportional to the difference between the incoming and exiting concentrations. Thus,

$$A_p = (c_i - p)(A_t/c_i) \qquad \text{(Eq. 4)}$$

After solving Equations 3 and 4 for p and equating them, the resulting equation can be rearranged as follows:

$$A_p = A_t \left(1 - \frac{1}{c_i \times 760}\right) \times 10^{\left[\frac{-0.2185\ A}{T + 273} + B\right]} \qquad \text{(Eq. 5)}$$

where A_p = predicted peak area count

A_t = calibrated area count for 100% trapping

A,B = tabulated parameters[8]

c_i = concentration of analyte entering trap (atm)

T = trap temperature (C)

Now a critical temperature (T_c) to predict 99% trapping efficiency (i.e., the temperature at which $A_p/A_t = 0.99$) can be derived from theoretical curves of A_p versus T at given input concentrations. An example of such a curve family is presented in Figure 1, in which predicted areas for benzene are plotted on a log scale versus trap temperature for input concentrations of 0.01, 0.1, 1.0, 10, and 100 ppbv. T_c, which is marked on each curve, is calculated by testing $(1 - A_p/A_t) < 0.01$ during the plotting routine.

Thus, empirical results can be directly compared to a prediction based on thermodynamic principles. Because the behavior of Equation 5 is similar for all compounds under consideration, only T_c will be quoted for the theoretical portion of subsequent comparisons.

Experimental Methods

The amount of trapped compound was measured with a capillary column equipped gas chromatograph and a flame ionization detector. The preconcentrator device regulated trap temperature to within ± 3C (or better) at any given setpoint in the range of -170C to +50C with a combination of feedback-controlled injections of liquid nitrogen and resistive heating. The trap consisted of 1/8-inch o.d. nickel tubing packed with 60 to 80 mesh pyrex beads. Sample flow was kept constant with a mass flow controller and diaphragm pump downstream of the trap. A volume of 1.5 ℓ was pulled through the trap for each analysis at a flow rate of 40 ml/min for 37.5 minutes. After the sampling valve was switched from collection to injection mode, the trapped compounds were desorbed at a maximum temperature of 125C onto an OV-1 column. With the exception of manual trap-temperature setpoint selection between runs, all sampling/analysis cycling was performed automatically under microprocessor control to achieve run-to-run consistency. A detailed description of this system can be found in Reference 9.

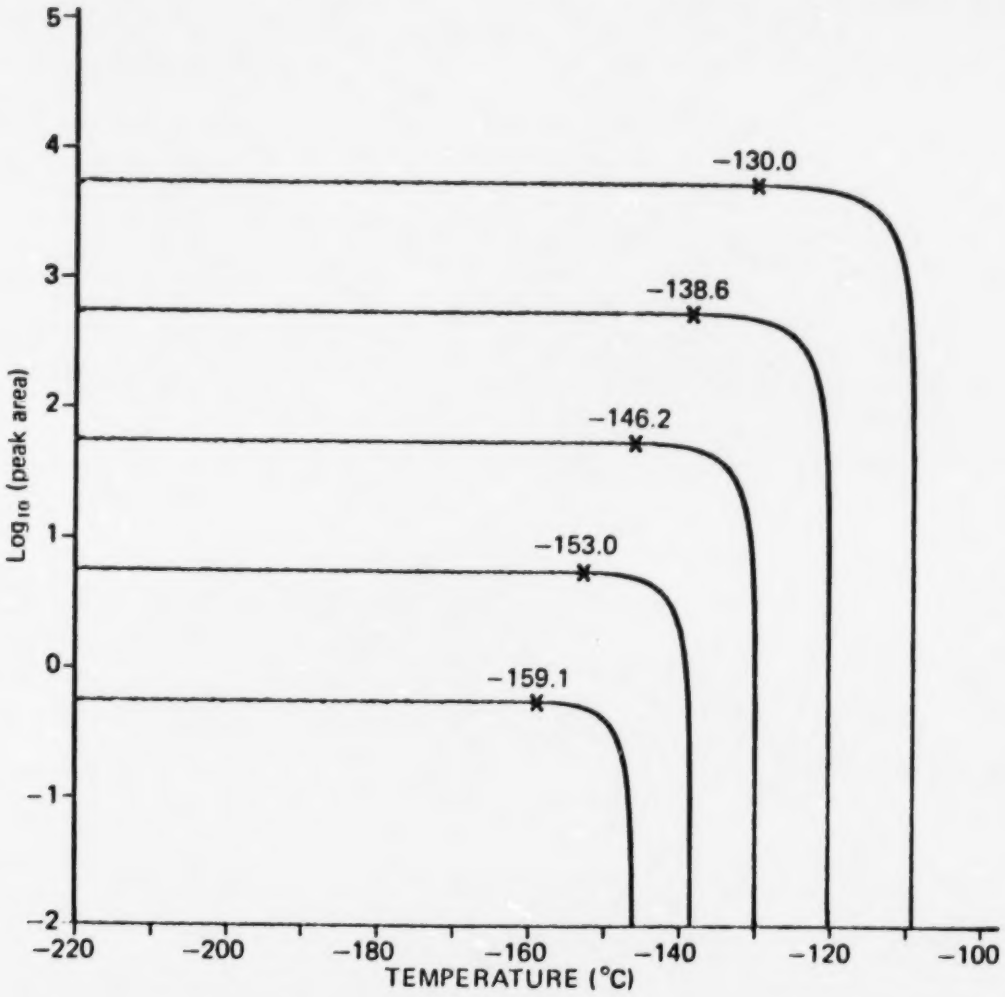

Figure 1. Theoretical curves for benzene, plotted as the base-10 logarithm of peak area versus temperature at which the compound was (theoretically) collected, according to Equation 5. Curves, from bottom to top, correspond to concentrations of 0.01, 0.10, 1.0, 10, and 100 ppbv. The critical temperature, defined as the point of 99% collection efficiency, is identified on each curve.

The contents, source, and VOC concentrations of six sample tanks used in this work are listed in Table I. Sample concentrations were prepared with a dynamic dilution system that used mass flow controllers and a dual stage, heated mixing manifold. Dilution ratios were periodically audited with bubble flowmeters. Trap temperature (as measured by a calibrated type-K thermocouple) was recorded on strip charts for verification of stability. Unlike ambient air, the samples prepared for these experiments were nominally water- and carbon dioxide-free.

As an example, the data set for benzene is graphed in Figure 2. The vertical axis is the base 10 logarithm of peak area in arbitrary but consistent units, and the horizontal axis is trap temperature in C. Data points are identified by sample concentration. Individual graphs for the remaining compounds are available in Reference 7.

The linear (horizontal) portion of data graphs similar to the example given in Figure 2 indicates the regime of 100% trapping efficiency. Table II contains an analysis of this data region for each compound and sampling concentration in which the number of data points, mean peak area, and standard deviation are given. In addition, a normalized detector reponse factor is calculated as follows:

$$R_n = A_m/(c_i \times V \times N) \qquad \text{(Eq. 6)}$$

where A_m = mean measured peak area

c_i = compound concentration sampled (ppbv)

V = volume sampled (cm^3)

N = number of carbon atoms per compound molecule.

This number (Rn) and its given percent standard deviation serve as indicators of run-to-run and concentration-dependent system stability. Note the many overlapping data points that appear as singles in the figures, particularly at -155C. These were taken for day-to-day quality control and are included in the statistical analyses of Table II.

Results and Discussion

Table III presents the reduced data of the experiments and the comparable theoretical values in terms of temperature necessary for "complete" trapping. For the experiment, this is defined as the point at which a data graph such as Figure 2 no longer shows an increase in compound collected for a further decrease in trap temperature. For the theory, this is arbitrarily defined as 99% collection efficiency, as shown in the example in Figure 1. Because the necessary constants were not available, there are no quoted theoretical values for the 1,3-dichloropropene isomers or for hexachlorobutadiene.

The data in Table III show a definite trend for efficient trapping at higher temperatures than estimates based solely on thermodynamic considera-

TABLE 1. CONTENTS OF SAMPLE TANKS USED FOR TRAPPING EFFICIENCY STUDIES

Tank No.	Identification and Comments	Compound	Nominal Concentration (ppm)
1	Prepared by Scott Specialty Gases, Tank #AAL-11078: Uncertified mixture in nitrogen	ethylene oxide	10.01
		pyridine	10.14
		o-xylene	10.06
		acrylonitrite	10.14
		toluene	10.09
		benzene	9.795
		propane	9.995
2	Prepared by Scott Specialty Gases, Tank #AAL-11074: Uncertified mixture in nitrogen	benzyl chloride	10.02
		1,3-dichloropropene*	10.19
		hexachlorobutadiene	9.951
		propane	9.996
		1,1,2-trichloro-1,2,2-trifluoroethane	10.10
		vinyl chloride	9.990
		dichloroethylene	10.05
		chloroform	10.03
		tetrachloroethylene	10.07
		dibromoethane	9.985
		chlorobenzene	9.984
		methyl chloroform	10.03
		carbon tetrachloride	10.04
		1,2-dichloroethane	10.11
		trichloroethylene	10.17
			(ppb)
3	Prepared by Battelle Columbus Laboratories: Unanalyzed mixture: Concentration accuracy quoted as ± 1% for benzene and ± 25% for the remaining compounds	1,1-dichloroethylene	151
		chloroform	84
		1,2-dichloroethane	44
		methyl chloroform	63
		benzene	93
		trichloroethylene	84
		tetrachloroethylene	69
		chlorobenzene	46

(continued)

TABLE 1. (continued)

Tank No.	Identification and Comments	Compound	Nominal Concentration (ppm)
4	Matheson: Analyzed mixture in nitrogen	acrylontrile	9.8
5	Matheson: Analyzed mixture in helium	benzene	6.8
6	Matheson: Analyzed mixture in ultra zero air	vinyl chloride	10.1

* Appears to have both cis and trans components for approximately equal concentrations.

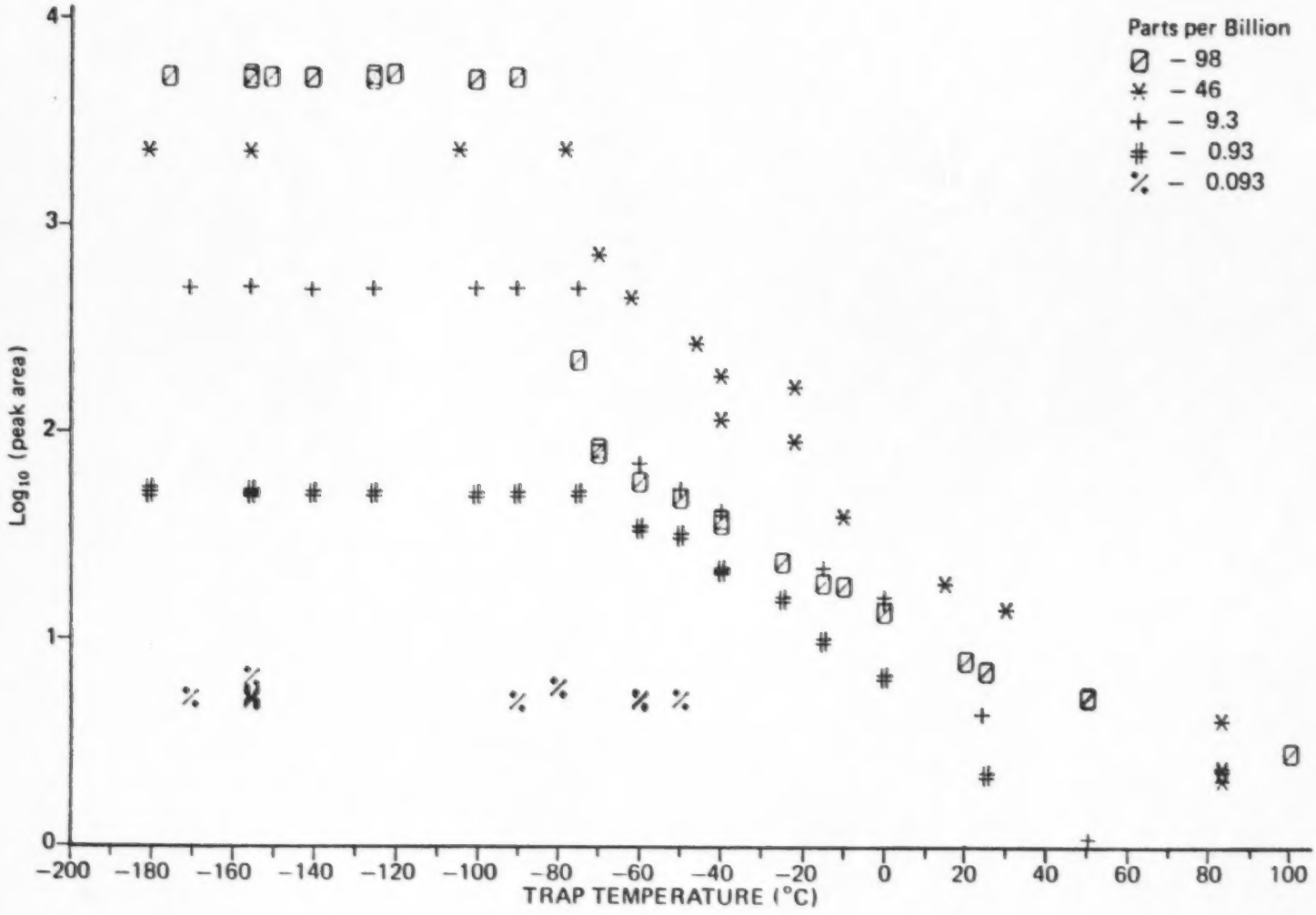

Figure 2. Experimental data for benzene, plotted as the base-10 logarithm of peak area versus temperature at which the compound was collected.

TABLE 2. STATISTICAL ANALYSIS OF DATA REGION REPRESENTING 100% COLLECTION EFFICIENCY FOR VARIOUS COMPOUNDS AT DIFFERENT CONCENTRATIONS

Compound	Tank No.	Concentration Sampled (ppbv)	No. Data Points	Mean Area	S.D Area	Response ($x10^3$)	Percent S.D. of Response
acrylonitrile	4	67	6	1155	62.22	3.83	5.39
	1	101	18	2092	65.14	4.60	3.11
benzene	3	0.093	15	5.46	0.4399	6.53	8.05
	3	0.93	15	51.76	0.891	6.18	1.72
	3	9.3	8	508.5	4.888	6.08	0.96
	5	46	4	2351	21.44	5.68	0.91
	1	98	17	5237.5	116.4	5.94	2.22
benzyl chloride	2	100	18	3686.1	1352	3.51	36.7
carbon tetrachloride	2	100	11	544.54	11.03	3.63	2.03
chlorobenzene	3	0.046	12	2.591	0.2230	6.26	8.61
	3	0.46	23	30.61	0.6177	7.39	2.02
	3	4.6	11	307.9	5.029	7.44	1.63
	2	99.8	14	5296.7	195.1	5.88	3.68
chloroform	3	0.084	15	0.9073	0.3920	7.20	43.21
	3	0.84	13	7.060	0.8497	5.60	12.04
	3	8.4	8	66.78	4.806	5.30	7.20
	2	100	13	649.7	15.32	4.33	2.36
1,2-dibromoethane	2	99.9	14	1682.6	76.56	5.61	4.55
1,2-dichloroethane	3	0.044	15	1.041	0.0499	7.89	4.79
	3	0.44	14	11.83	0.2901	8.96	2.45
	3	4.4	8	122.98	0.8600	9.32	0.70
	2	101	13	1929.1	21.11	6.37	1.09

(continued)

TABLE 2. (continued)

Compound	Tank No.	Concentration Sampled (ppbv)	No. Data Points	Mean Area	S.D Area	Response ($x10^3$)	Percent S.D. of Response
1,1-dichloroethylene	3	0.15	11	2.568	0.7403	5.71	28.83
	3	1.5	15	20.537	2.414	4.56	11.75
	3	15	7	185.99	2.270	4.13	1.22
	2	100	11	1895.3	31.61	6.32	1.67
1,3-dichloropropene (cis)	2	51	11	1402.3	42.72	6.11	3.05
1,3-dichloropropene (trans)	2	51	12	1143.5	74.59	4.98	6.52
ethylene oxide	1	100	18	657.06	37.28	2.19	5.67
hexachlorobutadiene	2	99.5	17	2442.1	347.8	4.09	14.24
methyl chloroform	3	0.063	15	1.208	0.08898	6.39	7.37
	3	0.63	14	13.089	0.3119	6.93	2.38
	3	6.3	8	130.519	1.690	6.91	1.29
	2	100	12	1946.6	23.79	6.49	1.22
pyridine	1	101	20	3211.2	701.1	4.24	21.8
tetrachloroethylene	3	0.069	15	1.613	0.0663	7.79	4.11
	3	0.69	20	17.543	0.5003	8.47	2.85
	3	6.9	8	173.09	1.654	8.36	0.96
	2	101	13	2037.5	32.29	6.72	1.58
toluene	1	101	17	6438.9	166.23	6.07	2.58
trichloroethylene	3	0.084	15	1.646	0.05221	6.53	3.17
	3	0.84	14	17.484	1.525	6.94	8.72
	3	8.4	8	173.12	3.343	6.87	1.93
	2	102	13	1953.8	21.47	6.38	1.10

(continued)

TABLE 2. (continued)

Compound	Tank No.	Concentration Sampled (ppbv)	No. Data Points	Mean Area	S.D Area	Response ($\times 10^3$)	Percent S.D. of Response
1,1,2-trichloro-1,2,2-trifluoroethane	2	101	11	1682.5	11.13	5.55	0.66
vinyl chloride	6	70	7	1190.5	3.1189	5.67	0.29
	2	100	11	1872.4	16.21	6.24	0.87
o-xylene	1	101	20	7146.2	325.9	5.90	4.56

TABLE 3. COMPARISON OF PREDICTED VERSUS EXPERIMENTALLY DETERMINED TRAP TEMPERATURES NECESSARY FOR COMPLETE TRAPPING OF VARIOUS COMPOUNDS AT DIFFERENT CONCENTRATIONS

Compound	Tank No.	Concentration Sampled (ppbv)	Predicted Temp. for 99% Trapping Efficiency (°C)	Experimental Temp. for Complete Trapping (°C)
acrylonitrile	4	67	-150	-40
	1	101	-149	-75
benzene	3	0.093	-153	>-50
	3	0.93	-146	-75
	3	9.3	-139	-75
	5	46	-133	-75
	1	98	-130	-90
benzyl chloride	2	100	-115	-15
carbon tetrachloride	2	100	-145	-125
chlorobenzene	3	0.046	-150	>-50
	3	0.46	-143	0
	3	4.6	-135	-40
	2	99.8	-122	-75
chloroform	3	0.084	-176	-60
	3	0.84	-170	-75
	3	8.4	-163	-75
	2	100	-155	-95
1,2-dibromoethane	2	99.9	-129	-75
1,2-dichloroethane	3	0.044	-172	>-50
	3	0.44	-166	-75
	3	4.4	-158	-75
	2	101	-147	-90
1,1-dichloroethylene	3	0.15	-180	>-80
	3	1.5	-175	-75
	3	15	-168	-75
	2	100	-162	-125
1,3-dichloropropene (cis)	2	51	NA	-90
1,3-dichloropropene (trans)	2	51	NA	-75
ethylene oxide	1	100	-169	-75
hexachlorobutadiene	2	99.5	NA	-25

(continued)

TABLE 3. (continued)

Compound	Tank No.	Concentration Sampled (ppbv)	Predicted Temp. for 99% Trapping Efficiency (°C)	Experimental Temp. for Complete Trapping (°C)
	3	0.063	-172	>-50
	3	0.63	-165	-75
methyl chloroform	3	6.3	-158	-75
	2	100	-149	-100
pyridine	1	101	-127	+25
tetrachloroethylene	3	0.069	-156	>-50
	3	0.69	-149	-40
	3	6.9	-141	-60
	2	101	-130	-90
toluene	1	101	-131	-75
trichloroethylene	3	0.084	-167	>-50
	3	0.84	-160	-75
	3	8.4	-153	-75
	2	102	-144	-90
1,1,2-trichloro-1,2,2-trifluoroethane	2	101	-160	-125
vinyl chloride	6	70	-178	-115
	2	100	-177	-125
o-xylene	1	101	-120	-70

tons. The range of behavior is spanned by carbon tetrachloride and pyridine: the former showed efficient trapping at -125C when -145C was predicted, and the latter showed essentially unchanged trapping to +25C when -127C was predicted. Also, for compounds for which concentrations spanning many orders of magnitude (1.0 to 100 ppbv) were measured, the higher concentrations were sometimes found to require lower trap temperatures. This effect was particularly pronounced in chlorobenzene and tetrachloroethylene. Theory predicted the opposite effect, as shown in the representative plots of Equation 5, given in Figure 1.

Both these deviations from the predicted behavior indicate a secondary trapping mechanism, presumably caused by active site bonding on the trap tubing or packing. Apparently these active sites become saturated at the higher concentrations; thus, equivalent trapping efficiencies required thermodynamic assistance in the form of lower trap temperatures. In all cases, however, the predicted temperatures were lower than the experimentally necessary value, which confirms the premise that a thermodynamic prediction can be accepted as a lower bound.

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